

Polymer Science at the NIST Combinatorial Methods Center

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INTRODUCTION

The measurements, standards, and test methods developed by NIST, in partnership with other organizations, often help unlock the potential of new discoveries and budding technologies. Combinatorial methods are a textbook example. These emerging tools can speed innovation in many fields - pharmaceuticals, chemistry, and, most recently, materials. In the diverse realm of materials, combinatorial methods hold promise for all classes, including metals, polymers, ceramics, and biomaterials. NIST has established a combinatorial methods center as a model for collaboration, in order to share expertise, facilities, resources, and information thereby reducing obstacles to participating in this fast-moving and instrument-intensive area. Although collaborations with multiple partners can be difficult, the goal is to foster cross-fertilization of ideas and research strategies, and to spur progress on many fronts by crossing boundaries of organizations, disciplines, and interests. A few examples of combinatorial project currently underway at NIST are in the areas of block copolymer ordering behavior, crystallization kinetics of polymers, quantitative polymer adhesion measurements, and phase separation as described below.

BLOCK-COPOLYMER ORDERING BEHAVIOR

The morphology of symmetric diblock copolymer thin films has been studied extensively with traditional techniques.^{1,2,3} Controlling the morphology of block co-polymers is important in designing polymeric materials with tailored properties since they can be used to produce nanoscale morphologies. For instance, their unique properties in melts, blends and solutions lead to their use in adhesives, emulsifying agents, thermoplastic elastomers, compatibilizers etc. Mechanisms for controlling block-copolymer morphology through surface induced orientation and preferential interactions are important issues.

Gradient libraries have been employed to revisit the well-studied phenomenon of lamella formation in symmetric diblock copolymers by analyzing the effect of film thickness on the morphology of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) thin films on Si substrates. Optical microscopy in conjunction with laser light scattering (under development) using temperature gradient stage in reflection and transmission geometry is expected to be the primary analytical tools for these high throughput studies. Figure 1 presents optical micrographs showing morphological changes associated with the addition of two lamellae to the surface of the film as the thickness (*h*) increases. The morphological evolution of the surface lamella with increasing film thickness has been observed within a single library allowing a significant reduction in experimental time. This combinatorial approach is found to be useful in discovering and characterizing new features of pattern formation in block copolymer films. Specifically, a range of film thickness were observed where the surface remains smooth up to a constant fraction of chain length independent of molecular mass that can be attributed to an increase in the surface chain density in the outer copolymer layer with increasing film thickness. Novel bicontinuous patterns are also observed whose average size scales as an inverse power of chain length.

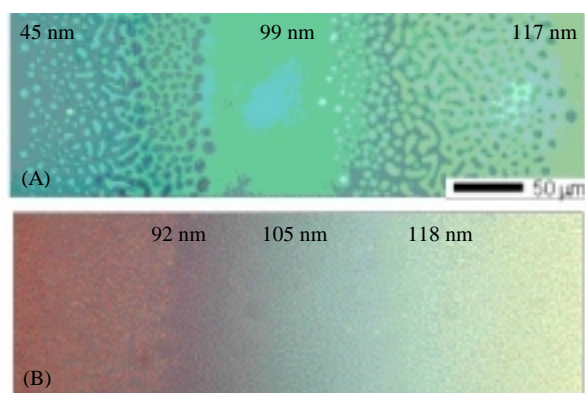


Figure 1. Optical micrograph of (A) $M_w=26,000$ g/mol and (B) $M_w = 104,000$ g/mol PS-*b*-PMMA gradient film showing the addition of lamellae to the surface with increasing thickness as indicated above. Standard uncertainty in thickness is ± 3 nm.

CRYSTALLIZATION KINETICS OF POLYMERS

The ability to direct or suppress order in polymeric thin films has many practical implications for industrial applications. In particular, the degree of crystallinity in semi-crystalline polymer films can be dramatically affected by a host of processing conditions such as solvents, thermal history, additives, etc. The challenge is to achieve desired mechanical, optical, or thermal properties in semi-crystalline thin film coatings by control of crystal structure and domain size. Developing a high-throughput method of screening these effects has the potential to quickly optimize the processing of materials, as well as probe many of the outstanding theoretical issues regarding the nature of polymer crystallization.⁴ One example is creating a gradient in film thickness and/or temperature in polymer films. High speed automated scanning methods such as optical and scanning force microscopy techniques can be used for evaluation of growth rate and other properties under orthogonally varying process variables such as temperature or stress gradients. Current research efforts have focused on factors affecting crystallinity in thin film coatings, specifically, the effect of temperature and film thickness on the morphology and kinetics of crystallization were examined. Utilizing flow coating film preparation, spot ellipsometry for thickness characterization and automated optical microscopy for imaging on a temperature gradient stage, complete libraries of the kinetics and morphology of high molecular mass isotactic polystyrene (*i*pS) on Si have been mapped in the course of a few hours. Typical optical micrograph images of *i*pS crystallizing are shown in Figure 2.

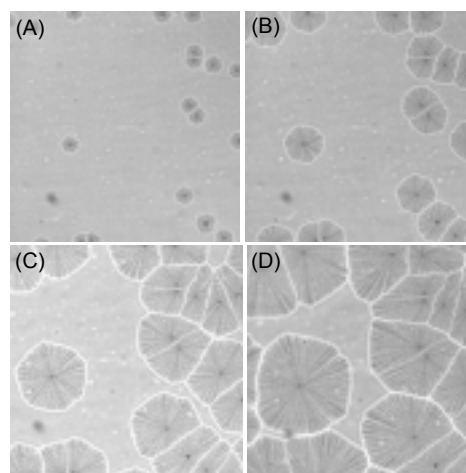


Figure 2. Optical images of *i*pS crystallizing at $T = 170$ °C. $h = 45$ nm, (A) $t = 21$ min, (B) $t = 51$ min, (C) $t = 96$ min, and (D) $t = 146$ min.

QUANTITATIVE POLYMER ADHESION MEASUREMENTS

Polymer adhesion is important to numerous technologies including electronic packaging, coatings and paints, biomedical implants, and pressure-sensitive adhesives. The challenge is to understand the fundamental driving forces for the development of adhesive strength at polymer/polymer, polymer/metal, polymer/ceramic, and polymer/biomaterial interfaces in multivariable environments. Current methods for characterizing adhesion are inefficient. The goal is to develop a methodology for quantitatively measuring the adhesive strength of polymer interfaces in a combinatorial manner. Combinatorial adhesion libraries consist of two components: 1) an array of microlenses with a well-defined geometry and 2) a flat sample. These libraries will present a unique combination of adhesion-controlling variables at each microlens contact point. By monitoring the contact area and relative displacement of each microlens during contact and separation from the sample, the adhesion energy can be mapped across the multivariable library. A combinatorial method has been developed and implemented to qualitatively and quantitatively map polymer interfaces to assess the dependence of anisotropic polymer adhesion on multivariable parameters. This technique allows us to not only identify optimal environments for the adhesion of given polymer interfaces, but also facilitates the fundamental investigation of how molecular structure and chemistry define adhesion. Current research efforts have focused on the design and preparation of the microlens combinatorial libraries, the instrumentation for controlling contact and separation, and the development of software to automate the data collection and analysis. Initial tests investigated the effect of thickness and temperature on the self-adhesion of polystyrene (PS). In this test, a microlens array was made from poly(dimethylsiloxane) (PDMS) shown in Figure 3. The self-adhesion of polystyrene validate the technique and demonstrate a thickness and temperature dependence for the adhesion of glassy polymer coatings.⁵ Current libraries yield the data equivalent of 1600 adhesion tests within the same time required for a single conventional adhesion test.

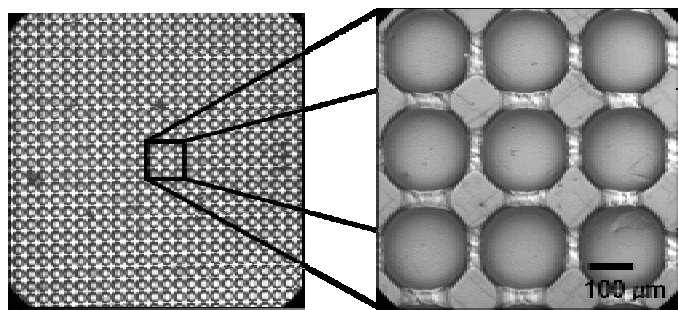


Figure 3. PDMS microlens array used for combinatorial adhesion tests.

POLYMER BLEND PHASE BEHAVIOR

The phase separation and related microstructure of polymer blends is of critical importance in many engineered plastics, but traditional determination of phase behavior for new blends, and blends with additives, remains a tedious task. Important factors influencing polymer blends phase behavior include effects of added compatibilizers, organic molecules, and inorganic fillers. Process variables such as temperature, supercritical fluids, in-situ reaction, polymerization, and cross-linking affect the thermodynamic and kinetic miscibility of polymer mixtures.

The approach is to develop combinatorial methodology for applying continuously varying composition gradients of miscible and immiscible polymer blends including additives, and utilize spectroscopic characterization techniques for quantitative determination of local composition, while measuring phase boundary by automated microscopy under typical applied processing conditions.

A composition-temperature phase boundary was evaluated and validated for polystyrene-poly(vinylmethyl ether) (PS/PVME) blend

systems. Figure 4 presents a photograph of a temperature-composition library of a PS/PVME blend after 16 h of annealing. The lower critical solution temperature (LCST) cloud point curve can be seen with the unaided eye as a diffuse boundary separating one-phase and two-phase regions. Cloud points measured with conventional light scattering on bulk samples (white points) agree well with the cloud point curve observed on the library.⁶ The diffuse nature of the cloud point curve reflects the dependence of the microstructure evolution rate on temperature and composition. A prototype composition mixing apparatus has been developed for this purpose, that also allows for the introduction of suspended nanoparticles and additives to study their effects on phase miscibility.

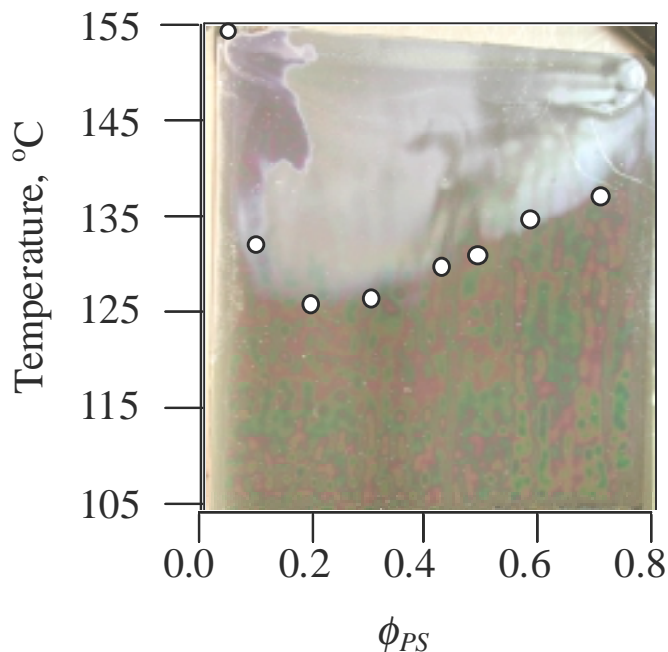


Figure 4. Optical photographs of a PS/PVME T- ϕ library after 16 h of annealing, showing the LCST cloud point curve visible to the unaided eye. White circles are conventional light-scattering cloud points measured on separate uniform samples.

ACKNOWLEDGEMENTS

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